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TITLE: Delamination resistant composites prepared by small diameter fiber reinforcement at ply interfaces

Brief Summary Text (26):

The diameter of conventional reinforcing fibers used in advanced composites typically varies from several micrometers up to hundreds of micrometers and even millimeters. Such conventionally employed fibers, include, for example, graphite, boron, glass, and ceramic fibers with diameters ranging to several hundred millimeters and even millimeters. In implementing the small diameter reinforcement of the present invention, generally, about one order of magnitude difference in diameter between the primary reinforcement fibers and the smaller secondary interlaminar reinforcement fibers will be sufficient. Where the primary reinforcement fibers are relatively large, fibers of conventional diameters (i.e., on the order of microns) are suitable for use as the secondary smaller interlaminar fibers. Where the primary reinforcement fibers are relatively small (i.e., micron range or smaller), then fibers of smaller diameters are needed to implement the concept described above. Therefore, depending on the diameter of the primary reinforcement fibers, fibers of submicron diameters (nanofibers) may be needed for interface reinforcement in accordance with the present invention.

Detailed Description Text (8):

The matrix material may also be thermoplastic materials based on acrylonitrile butadiene styrene (ABS) copolymers, aromatic polycarbonates, aromatic polyesters, carboxymethylcellulose, ethyl cellulose, ethylene vinyl acetate copolymers, polyacetals, polyacetates, polyacrylonitrile and other nitrile resins, polyacrylonitrile-vinyl chloride copolymer, polyamides, aromatic polyamides (aramids), polyamide-imide, polyarylates, polyarylene oxides, polyarylene sulfides, polyarylsulfones, polybenzimidazole, polybutylene terephthalate, polycarbonates, polyester imides, polyether sulfones, polyetherimides, polyetherketones, polyetheretherketones, polyethylene terephthalate, polyimides, polymethacrylate, polyolefins (polyethylene, polypropylene), polyallomers, polyoxadiazole, polyparaxylene, polyphenylene oxides (PPO), modified PPOs, polystyrene, polysulfone, polytetrafluoroethylene, polyvinyl acetate, polyvinyl alcohol, polyvinyl halides such as polyvinyl chloride, polyvinyl chloride-vinyl acetate copolymer, polyvinyl pyrrolidone, polyvinylidene chloride, specialty polymers, and so forth.

Detailed Description Text (16):

As stated above, fibers of smaller diameters relative to the primary reinforcement fibers are needed to implement the present invention. Thus, the diameter of the secondary reinforcement fibers will depend on the diameter of the primary reinforcement fibers. As stated above, the diameter of the secondary fibers is sufficiently small if it provides laminate interface reinforcement without substantial reduction of in-plane properties and/or without substantial increase in weight and/or ply thickness. Typically, the smaller diameter secondary fibers according to the present invention will generally have a diameter of approximately one-third, or less, of the diameter of the primary reinforcing fiber. In one embodiment, the diameter of the secondary reinforcement fiber will be about one-fourth, or less, of the diameter of the primary reinforcing fiber. In another embodiment, the diameter of the secondary reinforcement fiber will be about one-fifth, or less, of the diameter of the primary reinforcing fiber. In a most

preferred embodiment, there will be a difference of about one order of magnitude or greater between the primary and secondary reinforcement fiber diameters. Where the primary reinforcing fibers are of a relatively large diameter, secondary fibers of sufficiently small diameter may be obtained from conventional means or may otherwise be readily commercially available. When the diameter of primary reinforcing fibers themselves are relatively small in diameter, sufficiently small diameter secondary reinforcement fiber may have a more limited availability. For example, if it is desired to employ fibers having a diameter of several micrometers as the primary reinforcing fibers (such as graphite fibers having a diameter of about 5-7 micrometers as may be typically employed in advanced composites), then fibers of submicron diameters (hereinafter referred to as "nanofibers") will be required.

Detailed Description Text (17):

Several types of small diameter fibers are available. These include, but are not limited to, ceramic or metal whiskers, microdrawn metals, small carbon fibers, asbestos fibers, natural fibers such as cellulose and the like, and polymer fibers produced by air blowing, blend spinning, electrospinning, phase separation of copolymers or polymer blends, and so forth.

Detailed Description Text (18):

A new technology of manufacturing thin polymer fibers by electrospinning has been developed and studied. The method is based on the principle of spinning polymer solutions in a high-voltage electric field. It consists of the ejection, from the end of a capillary tube, of a charged jet of a liquid polymer, such as a polymer solution or molten polymer, which is elongated and accelerated by an external field. Nanofibers have been prepared by electrospinning from over thirty different synthetic and natural polymers, including high-temperature polyimide and polyaramid fibers. Electrospinning typically produces fibers having a diameter of about 5 to about 5000 nm, although fibers with diameters as small as three nanometers have been produced by this method. The method can be used to produce random nonwoven mats of fibers suitable for interface reinforcement. Any type of polymer can be electrospun to produce nanofibers, so long as it can be dissolved in an appropriate solvent or solvent mixture to make a concentrated solution (although in some cases the polymer melt may also be used) and the molecular weight is high enough. Table 1 below lists polymers that have been successfully electrospun into small diameter fibers.

Detailed Description Text (19):

References [8-10], each of which is incorporated herein by reference, disclose a number of methods for making superfine fibers. Wente [8] discloses a method of making submicron fibers via extrusion into heated, high velocity air streams. Reneker et al. [9] describe the electrospinning process. Reneker [10] discloses electrospinning as well as other methods for making small diameter fibers. FIG. 5 shows a random mat of electrospun polyimide fibers useful in reinforcing ply interfaces in accordance with the present invention. FIG. 6 shows a commercial Kevlar.RTM. fiber and electrospun Kevlar.RTM. fibers. Small diameter metal fibers such as nickel or steel fibers having diameters in the range of several microns as well as in the range of one micron and smaller are also available and are suitable for ply interface reinforcement. Likewise, submicron carbon and ceramic fibers, including short fibers (whiskers) are also commercially available and suitable for ply interface reinforcement in accordance with the present invention.

Detailed Description Text (22):

Although FIG. 1 is depicted in exploded view for illustrative purposes, the actual manner of construction may be accomplished in a number of ways. For example, one aspect of the present invention relates the modification of a conventionally formed or commercially supplied prepreg by placement of the secondary reinforcement fiber on the surface thereof. The manufacture of prepreps are generally known in the art and may be prepared, for example, by dipping the primary reinforcement fibers through a resin (i.e., solution), or, alternatively, by impregnating the primary reinforcement fibers through heat to melt the resin and pressure to force the resin into the fiber network. Once the prepreg is formed (or obtained commercially), the improved mat according to the present invention can be formed by attaching the secondary reinforcement fiber to the prepreg. In one embodiment, where the small diameter fibers are in the form of a mat, fabric, and so forth which can be handled, the small diameter fibers may be placed by hand on the prepreg. In another

embodiment, where the small diameter fibers are not in an easily handled form, for example, whiskers or short fibers not in a mat form, the fibers may be distributed over the surface of the prepreg, for example, from a gas or liquid suspension. In one embodiment, the short fibers may be distributed by spraying a gas, i.e., air, or liquid suspension thereof. In yet another embodiment, the secondary reinforcement fiber may be spun directly onto the surface of the prepreg using conventional spinning techniques, including electrospinning. In one embodiment, the fibers may be spun from a polymer solution, polymer melt, or from a fluid mixture of polymerizing reactants. In another embodiment, the fibers can be made by removal of the matrix after phase separation into fiber from a mixture containing dissolved polymer.

Detailed Description Text (24):

In a preferred embodiment, the present invention comprises a prepreg having a random mat of continuous electrospun fiber attached to one side of the prepreg. The mat may be separately formed by electrospinning and then simply placed onto one side of the prepreg. Alternatively, the secondary reinforcement fiber may be electrospun directly onto the prepreg. In either case, the prepreg will typically have sufficient tack such that no additional adhesive or resin will be necessary to maintain placement of the secondary reinforcement fiber on the prepreg surface.

Detailed Description Text (33):

Non-woven fabrics of polybenzimidazole (PBI) nanofibers with diameters ranging from 300-500 nanometers were manufactured by electrospinning. This temperature resistant, linear polymer with glass transition temperature about 430.degree. C. is used in thermal-protective, fire-blocking, and other aggressive temperature and environment applications. The sheets of electrospun PBI nanofibers were washed in water, treated with 50% sulfuric acid to improve the strength of the fibers, and dried at 200.degree. C. The areal weight of the resulting fiber mats was 6.85 g/m<sup>2</sup>. A scanning electron microscope (SEM) picture of the non-woven PBI sheet used in preparing the composites according to the present invention is shown in FIG. 2A.

Detailed Description Text (34):

Laminates with and without nanoreinforcement at interfaces were manufactured from a unidirectional graphite/epoxy prepreg T2G190/F263 provided by Hexcel Corporation. Unidirectional [0.sub.20] composite panels were manufactured. Strips of thin Teflon.RTM. film were placed as crack starters at the midplane interface. No additional epoxy resin was used during manufacturing of specimens with nanofibers. A specialized press-clave was designed and built for proper impregnation and consolidation of PBI nanofibers in the laminates. Several graphite/epoxy composite panels with nanofiber reinforcement of interfaces were manufactured in controlled temperature, pressure, and vacuum environments. Reasonable quality consolidation was confirmed by SEM observations of the cross-sections (FIG. 2B) and ultrasonic nondestructive evaluation.

Detailed Description Text (35):

The consolidated thickness of the nanoreinforced interlayer was around 21 micrometers. Volume content of nanofibers in the interlayer, calculated from the measured interlayer thickness, mat areal weight, and PBI density (1.4 g/cm<sup>3</sup>), was 24%. The consolidated thickness of the primary graphite/epoxy ply in the laminate without PBI nanofibers was around 180 micrometers. Therefore, less than 12% increase in the total laminate thickness is expected if the nanofibers were used at each interlaminar interface. Estimated increase in the laminate weight calculated as a ratio of the areal weights of the nanofiber sheet and the prepreg tape was 2.5%.

Detailed Description Text (41):

Ten or more fracture specimens were tested for each mode. The calculated values of the critical energy release rates for laminates with and without nanofiber reinforcement of interface are presented below. Increase of 130% in the Mode II and 15% in the Mode I critical energy release rates were observed, as shown in Table 2 below.

Detailed Description Text (42):

Optical images of the Mode I fracture surfaces of the specimens with nanoreinforced interface exhibited a variety of fracture modes including rather extensive intralaminar delamination. SEM images in FIGS. 3A and 3B show the transition from

the fracture through the nanoreinforced interlayer to the fracture in the resin rich zone between the nanoreinforced interlayer and the primary ply. Pulled out PBI nanofibers in FIG. 3B indicate their substantial mechanical strength. Longitudinal splitting in the primary ply, observed in FIG. 5, may have facilitated deviation of the interlaminar crack into the primary ply. Optical and SEM images of the Mode II fracture surfaces revealed the crack path primarily through the nanoreinforced interlayer or through the interface between the interlayer and the primary ply (FIGS. 4A and 4B). Some intralaminar fracture of the primary ply was also observed. The extent of intralaminar fracture varied from specimen to specimen. Analysis showed that specimens with considerable intralaminar fracture demonstrated lower  $G_{sub.IIc}$  values.

Detailed Description Text (56):

[9] Reneker et al., "Nanometer diameter fibers of polymer, produced by electrospinning," Nanotechnology, Vol. 7, pp. 216-23 (1996).

Detailed Description Text (57):

[10] Reneker, "Nanofibers for Engineered Textiles," UMIST--Textiles Engineered for Performance, Apr. 20-22, 1998.

Detailed Description Paragraph Table (1):

TABLE 1 Electrostatically Spun Polymers. Polymer Class Polymer Solvent High performance Polyimides Phenol polymers & liquid Polyamic acid m-Cresol crystal polymers Polyetherimide Methylene chloride Nylon 6 & Nylon 66 Formic Acid Polyaramid Sulfuric acid Poly-gamma-benzyl- Dimethylformamide (DMF) glutamate Poly(p-phenylene Sulfuric acid terephthalamide) Polybenzimidazole (PBI) dimethylacetamide (DMAC) Ultem 1000 (Polyether Chloroform imide) Copolymers Nylon 6-Polyimide Formic acid PET-PEN Trifluoroacetic acid/ dichloromethane Textile fiber Polyacrylonitrile Dimethylformamide polymers Polyethylene terephthalate Trifluoroacetic acid/ (PET) dichloromethane Polypropylene Melt in vacuum Nylon Formic acid Electrically Polyaniline Sulfuric acid conducting polymer Biopolymers DNA Water Polyhydroxybutyrate- Chloroform valerate Polyethers Polyethylene oxide Water & Water/ethanol (PEO) Polyesters Polynaphthalene Trifluoroacetic acid/ terephthalate (PEN) dichloromethane Polybutylene Trifluoroacetic acid/ terephthalate (PBT) dichloromethane Elastomers Styrene-butadiene rubber Tetrahydrofuran (THF) (SBR) Shell's Kraton (SBS) THF/DMF or Chloroform/DMF Other Polystyrene (PS) Toluene/DMF Polyacrylonitrile (PAN) DMF or DMAC Mesophase Pitch Melt spinning Polyvinyl chloride (PVC) THF/DMF Polyvinyl alcohol (PVA) Water

Other Reference Publication (8):

Reneker et al., "Nanometre diameter fibres of polymer, produced by electrospinning," Nanotechnology, vol. 7, pp. 216-223 (1996).

Other Reference Publication (9):

Reneker, "Nanofibers for Engineered Textiles," UMIST--Textiles Engineered for Performance, Apr. 20-22, 1998.

CLAIMS:

6. The laminate according to claim 1 wherein said secondary reinforcement fibers comprise one or more microfibers or nanofibers selected from the group consisting of metal fibers, carbon fibers, ceramic fibers, polymer fibers, and any combination thereof.

23. The prepreg according to claim 20 wherein said secondary reinforcement fibers comprise one or more microfibers or nanofibers selected from the group consisting of metal fibers, carbon fibers, ceramic fibers, polymer fibers, and any combination thereof.